Inter (Part-I) 2018

Chemistry	Group-II	PAPER: I
Time: 2.40 Hours	(SUBJECTIVE TYPE)	Marks: 68

SECTION-I

2. Write short answers to any EIGHT (8) questions: (16)

(i) How have 4.9 g of H_2SO_4 when completely ionized in water, produces equal number of positive and negative charges but the number of positively charged ions are twice than the number of negatively charged ions?

Ans 4.9 g of H_2SO_4 when completely ionized in water have equal number of positive and negative charges but the number of positively charged ions are twice the number of negatively charged ions.

$$\text{Moles of } H_2SO_4 = \frac{4.9}{98} = \frac{1}{20} = 0.05 \text{ moles}$$

$$\begin{array}{ccccc} H_2SO_4 & \rightleftharpoons & 2H^+ & + & SO_4^{-2} \\ 4.9\text{ g} & & 2 \times 0.05 & & 0.05 \\ (0.05\text{ moles}) & & \text{moles} & & \text{moles} \end{array}$$

4.9 g of H_2SO_4 (0.05 moles) when ionized completely, produces 0.1 moles of positively charges and 0.1 moles of negative charges. Hence, no. of positive and negative charges are same 4.9 g of H_2SO_4 (0.05 moles) produces 0.1 moles of H^+ ion and 0.05 moles of SO_4^{-2} ions. Hence, no. of positively charged ions are twice than the no. of negatively charged ion.

(ii) How has one mg of K_2CrO_4 thrice the number of ions than the number of formula units when ionized in water?

Ans One mg of K_2CrO_4 has thrice the number of ions than the number of formula units when ionized in water.

$$K_2CrO_4 \xrightleftharpoons{H_2O} 2K^+ + CrO_4^{-2}$$

This equation shows that 1 mg formula unit of K_2CrO_4 ionizes into three ions (2 K^+ and 1 CrO_4^{-2}). Hence, the number

of ions is thrice the no. of formula units of K_2CrO_4. One mg will have same value.

(iii) Why do 2 g of H_2, 16 g of CH_4, 44 g of CO_2 occupy separately the volume of 22.414 dm^3 although the sizes and masses of molecules of three gases are very different from each other?

Ans 2 g of H_2:

1 mole of H_2 = 6.02×10^{23} molecules of H_2

16 g of CH_4:

1 mole of CH_4 = 6.02×10^{23} molecules of CH_4

144 g of CO_2

1 mole of CO_2 = 6.02×10^{23} molecules of CO_2

Though H_2, CH_4 and CO_2 have different masses, yet they have the same number of moles and molecules. Therefore, 2 g of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3.

(iv) How does rate of filtration increase by using fluted filter paper?

Ans The rate of filtration through conical funnel can be considerably increased using a fluted filter paper. For preparation of such a paper, ordinary filter paper is folded in such a way that a fan-like arrangement with alternate elevations and depressions at various folds is obtained.

(v) Name the various experimental techniques which are used for purification of substances?

Ans Various experimental techniques which are used for the purification of substances are given below:

1. Filtration 2. Crystallization
3. Sublimation 4. Solvent Extraction

(vi) Derive expression of density of gas with the help of general gas equation.

Ans For calculating the density of an ideal gas, we substitute the value of number of moles (n) of the gas in terms of the mass (m), and the molar mass (M) of the gas.

$$n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT \qquad \text{(i)}$$

Equation (i) is another form of general gas equation that may be employed to calculate the mass of gas, whose P, T, V and molar mass are known.

Rearranging equation (i),

$$PM = \frac{m}{V} RT$$

$$PM = d\,RT \qquad (d = \frac{m}{V})$$

$$d = \frac{PM}{RT}$$

Hence, density of an ideal gas is directly proportional to its molar mass.

(vii) Write two characteristics of plasma state.

Ans Following are the two characteristics of plasma state:

1. A plasma must have sufficient number of charged particles. So, as a whole, it exhibits a collective response to electric and magnetic field.
2. Although, plasma includes electrons and ions and conducts electricity, it is macroscopically neutral. In measurable quantities, the number of electrons and ions are equal.

(viii) Calculate value of the general gas constant (R) in unit of dm^3 atm K^{-1} mol^{-1}.

Ans

$$R = \frac{PV}{nT}$$

Putting their values, along with units,

$$R = \frac{1 \text{ atm} \times 22.414 \text{ dm}^3}{1 \text{ mole} \times 273.16 \text{ K}}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

(ix) Why do the rate of forward reaction slow down when a reversible reaction approaches the equilibrium stage?

Ans Rate of reaction is directly proportional to molar concentration (active masses) of reactants. At start, concentration of reactants is maximum and rate of reaction is faster. When equilibrium is approached, the concentration of reactants is small

as most of it is converted to products. Hence, the rate of forward reaction is slow due to low concentration of reactants.

(x) Prove by equations that what happens when Na_2CrO_4 is added to saturated solution of $PbCrO_4$?

Ans Consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_{4\,(aq)}^{2-}$$

Now, add Na_2CrO_4, which is a soluble salt. CrO_4^{2+} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$.

(xi) Define Lowry-Bronsted concept of acids and bases.

Ans According to this concept, acids are those species which donate the proton or have a tendency to donate, and bases are those species which accept the proton or have a tendency to accept the proton.

(xii) What is the formula to calculate the percentage ionization of weak acid?

Ans The formula to calculate the percentage ionization of weak acid is give below:

$$\%\ \text{ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

3. Write short answers to any EIGHT (8) questions: (16)

(i) Why boiling point of H_2O is different at Murree Hills and at Mount Everest?

Ans At sea level, atmospheric pressure is 760 torr and boiling point of water is 100°C. By reducing external pressure, the boiling point also reduces. As we go at higher altitude, atmospheric pressure decreases. Atmospheric pressure at Mount Everest is less than at Murree Hills. At Murree Hills, atmospheric pressure is 700 torr and boiling point of water is 98°C but at Mount Everest water boils at 69°C (atmospheric pressure = 323 mm Hg).

(ii) Define transition temperature. Give two examples.

Ans It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At

this temperature, one crystalline form of a substance changes to another.

Example:

$$Na_2SO_4 \cdot 10H_2O \text{ (hydrated form)} \xrightleftharpoons{32.38^\circ C} \underset{\text{(anhydrous form)}}{Na_2SO_4} + 10H_2O$$

$$\underset{\text{(orthorhombic)}}{KNO_3} \xrightleftharpoons{128^\circ C} \underset{\text{(rhomboclinic)}}{KNO_3}$$

(iii) Why does ice float on water?

Ans It is because the chemical bonds between H_2O molecules are forced into being longer, expanding the water and forming a crystal. When something is at constant mass, it increases in volume, its density decreases. Thus, ice is less dense than water causing it to float.

(iv) What are Debye forces?

Ans The Debye force is the results from the interaction between the permanent dipoles of polar molecules and the dipoles. They may induce in similar molecules and in initially non-polar molecules.

(v) Define the term bond order with one example.

Ans **Bond order:**

The no. of bonds formed between two atoms, after atomic orbitals overlap, is called bond order. It is taken as half of difference between the no. of bonding and anti-bonding electrons.

Bond order of H-atom:

No. of electrons in bonding orbitals = 2

No. of electrons in anti-bonding orbitals = 0

$$\text{Bond order} = \frac{2-0}{2}$$

$$= 1$$

(vi) Ionization energy is an index to the metallic nature of element. Justify.

Ans Ionization energy is an index to the metallic character. The element having low ionization energies are metals and those having high ionization energies are non-metals. Those with intermediate values are mostly metalloids.

(vii) 75.4 pm is compromise distance between the bonded hydrogen atoms. Justify.

Ans In the formation of H_2 molecule, potential energy decreases as the two hydrogen atoms approach each other.

Eventually, a state corresponding to the distance of 75.4 pm is reached, where the attractive forces dominate the repulsive forces. Here, the potential energy of the system is minimum and the hydrogen atoms are said to be bonded to form a stable. So, this distance of 75.4 pm is called bond distance or compromise distance of two hydrogen atoms.

(viii) Why is no bond in chemistry 100% ionic?

Ans The maximum electronegativity difference between the two bonded atoms is 3.2, *i.e.,* CsF and the %age of ionic character as per Pauling's formula in CsF is 92 %. So ,no bond in chemistry is 100 % ionic.

(ix) Burning of candle is spontaneous process. Explain.

Ans Spontaneous process is defined as: "Once it is allowed to start, the process will proceed to the finish without any external intervention." You lit the candle, it was allowed to burn and it would keep going without any help. Thus, candle burning is a spontaneous process.

(x) Define enthalpy of solution and enthalpy of neutralization.

Ans **Enthalpy of solution:**

The standard enthalpy of a solution is the amount of heat absorbed or evolved, when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change.

Enthalpy of neutralization:

The standard enthalpy of neutralization is the amount of heat evolved, when one mole of hydrogen ions $[H]^+$ from an acid, react with one mole of hydroxide ions from a base to form one mole of water.

(xi) Define upper consulate temperature. Give two examples.

Ans Upper consulate temperature is the critical temperature above which the components of a mixture are miscible in all proportions.

For example, palladium-hydrogen system has a solution phase in equilibrium with a hydride phase below at 300°C. Above this temperature, there is a single solid solution phase.

(xii) Give two statements of Raoult's law.

Ans **Raoult's Law:**

First Statements:

The vapour pressure of solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.

$$\Delta p = p^o x_2$$

Second Statement:

The lowering of vapour pressure is directly proportional to the mole fraction of the solute.

4. Write short answers to any SIX (6) questions: (12)

(i) State Pauli's exclusion principle and Hund's rule.

Ans According to Pauli Exclusion Principle, two numbers in the same orbital should have opposite spins (↓↑). On the other hand, according to Hund's rule, if degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

(ii) Calculate the number of electrons in s, p, d and f sub-shells from the formula and write separately.

Ans 'l' values enable us to calculate the total number of electrons in a given subshell. The formula for calculating electrons is $2(2l + 1)$.

When	$l = 0$	s-subshell	total electrons = 2
	$l = 1$	p-subshell	total electrons = 6
	$l = 2$	d-subshell	total electrons = 10
	$l = 3$	f-subshell	total electrons = 14

(iii) Write down any two postulates of Planck's quantum theory.

Ans Two postulates of Planck's theory are:

1. Energy is not emitted or absorbed continuously. Rather, it is emitted or absorbed in a discontinuous manner and in the form of wave packets. Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is often called photon.

2. The amount of energy associated with a quantum of radiation is proportional to the frequency (ν) of the radiation. Frequency is the number of waves passing through a point per second.

$$E \propto \nu$$

$$E = h\nu$$

(iv) Why is e/m value of the cathode rays just equal to that of electron?

Ans Cathode rays consist of streams of negatively charged particles called electrons. The e/m value of cathode rays shows that they are simply electrons. Therefore, this value for cathode rays is just equal to that of electrons.

(v) What is electrochemistry?

Ans Electrochemistry is concerned with the conversion of electrical energy into chemical energy in electrolytic cells as well as the conversion of chemical energy into electrical energy in galvanic or voltaic cells.

(vi) Write down the function of salt bridge.

Ans The purpose of salt bridge is to prevent any net charge accumulation in either beaker by allowing negative ions to leave the right beaker, diffuse through the bridge and enter left beaker. If this exchange does not occur, net charge accumulating in beakers would immediately stop the flow of electrons through the external circuit and redox reaction would stop.

(vii) A porous plate or salt bridge is not required in lead storage cell. Why?

Ans A porous plate or salt bridge is used in those cells where two different electrolytes are used and are required to kept separate. In case of lead storage cell, only dil. H_2SO_4 is used as an electrolyte. Hence, no separation is required by porous plate or salt bridge.

(viii) The radioactive decay is always the first order reaction, give reasons.

Ans Radioactive substances have a single species at a moment, whose nucleus is being broken up without the help of any external agency. So, only one reactant is present and it follows the first order mechanism.

(ix) How are enthalpy changes of reaction and energy of activation of reaction distinguished?

Ans

Enthalpy Change of Reaction	Energy of Activation of Reaction
1. Heat change accompanied by chemical reaction is called enthalpy change.	1. The minimum amount of energy in addition to average K.E. sufficient to convert reactants into products is called activation energy.
2. It is denoted by ΔH.	2. It is denoted by E_a.
3. It may be negative or positive.	3. It is always positive.

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) Ethylene glycol is used as automobile antifreeze. It has 38.7% C, 9.7% hydrogen and 51.6% oxygen. Determine its empirical formula. (4)

Ans For Answer see Paper 2017 (Group-I), Q.5.(a).

(b) How vapour pressure can be measured by manometric method? Explain with diagram. (3,1)

Ans **Measurement of Vapour Pressure:**

There are many methods for the measurement of vapour pressure of a liquid. One of the important methods is described in the following paragraph:

Manometric method:

Manometric method is comparatively an accurate method. The liquid whose vapour pressure is to be determined, is taken in a flask placed in a thermostat, as shown in the Fig. One end of the tube from the flask is connected to a manometer and the other end is connected to a vacuum pump. The liquid is frozen with the help of a freezing mixture and the space above the liquid is evacuated. In this way, the air is removed from the surface of the liquid along with the vapours of that liquid. The frozen liquid is then melted to release any entrapped air. Liquid is again frozen and released air is evacuated. This process is repeated many times till almost all the air is removed.

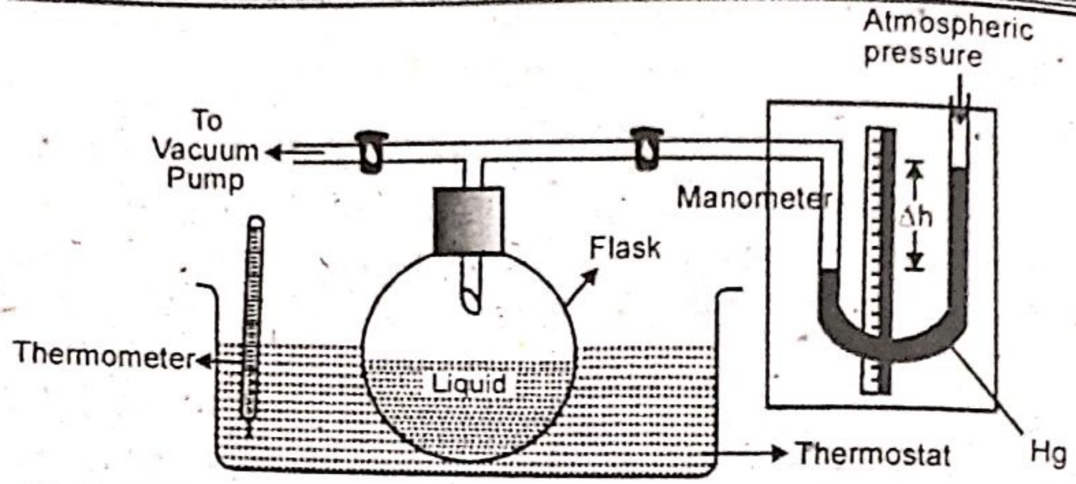

Fig. Measurement of vapour pressure of a liquid by manometric method.

Now, the liquid is warmed in the thermostat to that temperature at which its vapour pressure of the liquid in the flask is to be determined. Difference in the heights of the columns of Hg in the two limbs of the manometer determines the vapour pressure of the liquid.

The column of mercury in the manometer facing the vapours of the liquid is depressed. The other column, which faces the atmospheric pressure, rises. Actually, the pressure on the surface of the liquid in the flask is equal to the sum of the atmospheric pressure and the vapour pressure of liquid. For this reason, the column of manometer facing the liquid is more depressed than facing the atmosphere, and it is given by the following equation

$$P = P_a + \Delta h$$

Where P = Vapour pressure of the liquid at one atm pressure.

P_a = Atmospheric pressure.

Δh = Difference in the heights of the mercury levels in the two limbs of the manometer, giving us the vapour pressure of liquid.

Q.6.(a) Explain Linde's method of liquefaction of gases. (4)

Ans Linde's Method:

Linde has employed Joule-Thomson effect as the basis for liquefaction. For the liquefaction of air, it is compressed to

about 200 atmospheres, and then passed through a water cooled pipe where the heat of compression is removed. It is then allowed to pass through a spiral pipe having a jet at the end. When the air comes out of the jet, the expansion takes place from 200 atm to 1 atm. In this way, considerable fall of temperature occurs. This cooled air goes up and cools the incoming compressed air. It returns to the compression pump. This process is repeated again and again. The liquid air is collected at the bottom of the expansion chamber. All gases except H_2 and He (Neon) can be liquefied by the above procedure.

(b) Write down the four properties of neutron. (4)

Ans Properties of Neutron:

(i) Free neutron decays into a proton ($^{1}_{+}P$) with the emission of an electron ($^{0}_{-1}e$) and a neutrino ($^{0}_{0}n$).

$$^{1}_{0}n \longrightarrow {}^{1}_{+1}P + {}^{0}_{-1}e + {}^{0}_{0}n$$

(ii) Neutrons cannot ionize gases.

(iii) Neutrons are highly penetrating particles.

(iv) They can expel high speed protons from paraffin, water, paper and cellulose.

Q.7.(a) How does molecular orbital theory explain the paramagnetic character of O_2 molecule? Also calculate the bond order. (4)

Ans Oxygen O_2:

The formation of molecular orbitals in oxygen molecule is shown in Fig.

The electronic configuration O2 is

$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x) < \pi(2p_y)^2 = \pi(2p_z)^2 <$
$\pi^*(2p_y)^1 = \pi_z^*(2p_z)^1 < \sigma^*2p_x$

The bond order in O_2 is $\frac{6-2}{2} = 2$, which corresponds to a double bond.

This is consistent with the large bond energy of 496 kJ. mol^{-1} of oxygen molecule.

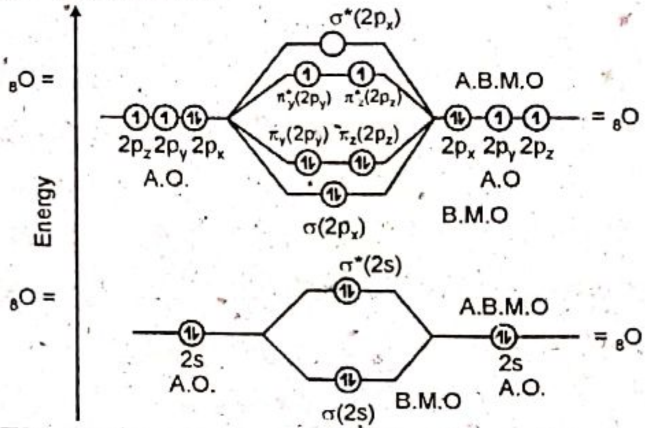

Fig. Molecular orbitals in O_2 molecule.

Fig. shows that the filling of molecular orbitals leaves two unpaired electrons in each of the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ orbitals. Thus, the electronic configuration of the molecular orbitals accounts admirably for the paramagnetic properties of oxygen. This is one of the greatest successes of the molecular orbital theory. Liquid O_2 is attracted towards the magnet.

Anyhow, when two more electrons are given to O_2, it becomes O_2^{2-}. The paramagnetism vanishes. Similarly, in O_2^{2+}, the unpaired electrons are removed and paramagnetic property is no more there. Bond order of O_2^{2-} and are also different from O_2 and are one and three, respectively.

Similarly, M.O.T justifies that F_2 has bond order of one and Ne does not make a bond with Ne.

(b) State first law of thermodynamics. How does it explain that $q_p = \Delta H$? (4)

Ans For Answer see Paper 2016 (Group-I), Q.7.(a).

Q.8.(a) What is common ion effect? How is this effect used in salt analysis? Give two examples. (4)

Ans **Common Ion Effect:**

The suppression of ionization of a weak electrolyte by adding a common ion from outside, is called common ion effect.

We are familiar with purification of sodium chloride by passing hydrogen chloride gas through saturated brine. Sodium

chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl]}$$

HCl also ionizes in solution

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

On passing HCl gas, concentration of Cl^- ions is increased, therefore, $NaCl$ crystallizes out of the solution to maintain the constant value of the equilibrium constant.

This type of effect is called the common ion effect. The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl(s)$$

Examples:

(i) The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO^-_{3(aq)}$$

$$KCl \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

(ii) Similarly, the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way, low concentration of S^{-2} ion is developed.

$$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

This low concentration of S^{-2} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

(b) **Give explanation of discharging and recharging of lead accumulator, along with reactions occurring at electrode. (4)**

Ans For Answer see Paper 2017 (Group-I), Q.8.(a).

Q.9.(a) The boiling point of water is 99.725°C. To a sample of 600 g of water are added 24.0 g of a solute having molecular mass of 58 g mol^{-1}, to form a solution. Calculate the boiling point of the solution. (4)

Ans Boiling point of pure H_2O = 99.725°C

Mass of solvent (H_2O) W_1 = 600 g

Mass of solute (W_2) = 24.00 g

Molar mass of solute (M_2) = 58 g mol^{-1}

The molal boiling point constant of $H_2O(K_b)$ = 0.52°C

Formula: $$\Delta T_b = K_b \times \frac{1000\ W_2}{W_1 \times M_2}$$

$$= \frac{0.52 \times 1000 \times 24.00}{600 \times 58} = 0.358°C$$

Boiling point of solution = Boiling point of pure solvent + Elevation of boiling point

$$= 99.725 + 0.358 = \boxed{100.083°C}$$

(b) **Define order of reaction and explain 2nd and zero order reaction. (4)**

Ans **Definition:**

The order of reaction is the sum of exponents of the concentration terms in the rate equation.

Zero Order Reaction:

That chemical reaction, whose rate is independent of concentration of reactant, is called zero order reaction.

Characteristics of zero order reaction:

(i) The change of concentration of product has a linear relationship with time.

(ii) The unit of rate constant is mole dm^{-3}s^{-1}which is unit of rate of reaction.

(iii) The half-life period is $\frac{a}{2}$.

Examples of zero order reaction:

(i) Photochemical combination of H_2 and Cl_2 to give HCl, when carried out over water surface is a zero order reaction.

(ii) Decomposition of ammonia by using tungsten.

$$2NH_3 \xrightarrow{\text{Tungsten}} N_2 + 3H_2$$

(iii) The thermal decomposition of HI on gold surface.

$$2HI \xrightarrow{\text{Gold}} H_2 + I_2$$

(iv) The reactions which are catalyzed by enzymes also obey the zero order kinetics.

Second order reaction:

(i) Decomposition of HI in the gas phase

$$2HI \longrightarrow H_2 + I_2$$

Rate of reaction = $k[HI]^2$

(ii) Decomposition of ozone.

$$2O_3 \longrightarrow 3O_2$$

Rate of reaction = $k[O_3]^2$

(iii) Decomposition of CH_3CHO.

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO$$

Rate of reaction = $k[CH_3CHO]^2$